

# Electrochemical technology enables nutrient recovery and ammonia toxicity control in anaerobic digestion

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## Abstract

The aim of this study was to investigate the impact of an electrochemical system (ES) on the performance of an anaerobic digester during both low and high ammonium ( $\text{NH}_4^+$ ) loading rates. For this, a Test (with ES) and Control (without ES) setup was used. Ammonia ( $\text{NH}_3$ ), in equilibrium with  $\text{NH}_4^+$ , is a toxic compound to the methanogenic community, limits the substrate loading rate and endangers process stability. We hypothesized that, through coupling of an ES to a digester,  $\text{NH}_3$  toxicity can be controlled with simultaneous recovery of this nutrient. The ES always had a temporary negative effect when switched on. However, during periods of high ammonium loading rates the  $\text{CH}_4$  production of the Test reactor was at maximum a factor 4.5 higher compared to the Control reactor, which could be explained through a combination of  $\text{NH}_4^+$  extraction and electrochemical pH control. A nitrogen flux of  $47 \text{ g N m}^{-2} \text{ membrane d}^{-1}$  could be obtained in the Test reactor, resulting in a current and removal efficiency of  $38 \pm 5\%$  and  $28 \pm 2\%$ , respectively. For this, an electrochemical power input  $17 \pm 2 \text{ kWh kg}^{-1} \text{ N}$  was necessary. In addition, anodic oxidation of sulphide resulted in a significantly lower  $\text{H}_2\text{S}$  emission.

**Keywords:** ammonium recovery; cation exchange membrane; electrochemical system; membrane electrolysis; methanogenesis

## Introduction

Electrochemical systems (ES) have the attractive feature that an oxidation process (anode) is separated from a reduction process (cathode), typically by an ion selective membrane. By applying a current to this system, membrane electrolysis can take place in which ions can be extracted from anode to cathode or vice versa. In the context of wastewater treatment this leads to applications enabling recovery of valuable nutrients such as ammonium ( $\text{NH}_4^+$ ) and potassium ( $\text{K}^+$ ). In our opinion, this technology is particularly useful in combination with anaerobic digestion (AD). The latter is generally considered as a key technology for stabilisation and valorisation of organic waste streams (Mata-Alvarez *et al.*, 2000, Verstraete *et al.*, 2005). Anaerobic digestion allows the conversion of low-value organic compounds into biogas, a mixture of methane ( $\text{CH}_4$ ) and carbon dioxide ( $\text{CO}_2$ ). Methane is an energy carrier and can be valorised through e.g. combined heat and power, delivering electricity and heat. Despite numerous advantages of the AD process, instability is an often-encountered problem that can lead to complete failure of the reactor. One of the key compounds able to cause instability is ammonia ( $\text{NH}_3$ ). It has been widely documented that methanogens, responsible for the final step in the anaerobic digestion process, have a moderate tolerance to this molecule (Chen *et al.*, 2008). This toxicity issue, inherent to the digestion of nitrogenous material, exposes digesters to a risk of process instability and limits the loading and thus biogas production rate (Angelidaki and Ahring, 1993). Hence, by combining AD with ES technology, nutrients can be harvested whilst simultaneously lowering ammonia toxicity.

We have recently demonstrated the proof of concept of an electrochemical cell for nutrient recovery from liquid waste streams (Desloover *et al.*, 2012). In this study, we present the direct coupling of an ES to an Upflow Anaerobic Sludge Blanket (UASB) reactor for combined control of ammonia toxicity and nutrient recovery. We hypothesize that an ES has no negative effect on the AD process, and significantly improves the AD performance when exposed to toxic  $\text{NH}_3$  concentrations.

## Material and Methods

### *Experimental setup*

Two cylindrical UASB reactors (2.3 L glass reactor with effective volume of 2 L) were constructed, serving as a Test and Control reactor. For the Test reactor, an ES was coupled to the UASB for extraction of cations. This was done by inserting the anode compartment ( $5 \times 20 \times 2 \text{ cm}^3$ ) of the ES in the recirculation loop of the UASB reactor. The anode compartment was separated from the cathode compartment ( $5 \times 20 \times 2 \text{ cm}^3$ ) by a Cation Exchange Membrane (CEM, Membranes International, USA). The anode electrode used was an IrOx coated titanium electrode ( $5 \times 20 \text{ cm}^2$ , Magneto Special Anodes, The Netherlands) whilst the cathode electrode was Stainless Steel Mesh ( $5 \times 20 \text{ cm}^2$ , mesh width  $564 \mu\text{m}$  Solana, Belgium). At the anode, water was oxidized to oxygen whilst at the cathode water was reduced to hydrogen gas and hydroxyl ions. The ES was controlled galvanostatically by a Potentiostat (Biologic, France). The Control reactor was also equipped with an ES in the recirculation loop. However in this case the ES was operated in open circuit, meaning that no current was applied to the system and only diffusion driven processes could take place.

### *Reactor operation*

The experiment was conducted under mesophilic conditions ( $34^\circ\text{C}$ ). The UASB reactors were inoculated with granular sludge from a full-scale UASB reactor (Brewery Van Steenberge, Belgium) and diluted with tap water to obtain a starting sludge concentration of  $10 \text{ g Volatile Suspended Solids (VSS) L}^{-1}$ . The UASBs were fed every 2h with diluted molasses according to the desired loading rate and were operated at a hydraulic retention time (HRT) of 2 days. Furthermore, an internal recirculation rate was applied over the UASB and anode compartment of  $2 \text{ L h}^{-1}$  to maintain an upflow velocity of  $1 \text{ m h}^{-1}$  in the digester. In order to maintain the same conductivity throughout the experimental period, NaCl was initially added to the feed to compensate for any later on addition of  $\text{NH}_4\text{Cl}$  when the performance was investigated under high nitrogen loading conditions (Table 1). Both reactors were pH controlled (Dulcometer D1C, Prominent, Germany) with  $1 \text{ M NaOH}$ .

The cathode compartments of the Control and Test setup were fed continuously with  $6.4 \text{ g L}^{-1}$  NaCl at  $1 \text{ L d}^{-1}$  (HRT of 4.8 h) with an internal recirculation rate of  $2 \text{ L h}^{-1}$ .

### *Experimental plan*

The experimental plan comprised 4 main phases (Table 1). During Phase I the organic loading rate was gradually increased from  $1$  to  $5 \text{ g COD Lr}^{-1} \text{ d}^{-1}$  (Phase Ia). After stable operation, the pH was stepwise ( $0.25 \text{ pH units per week}$ ) increased from  $7$  to  $8$  (Phase Ib) to shift the  $\text{NH}_4^+/\text{NH}_3$  equilibrium more to the direction of  $\text{NH}_3$  (ratio  $\text{NH}_3/\text{NH}_4^+ = 0.11$  at pH  $8$  and  $34^\circ\text{C}$ ). Next, the ES of the Test setup was switched on at an applied current density of  $10 \text{ A m}^{-2}$  to investigate the impact during low nitrogen loading. At day 120, the UASB of the Test setup crashed due to a malfunction of the pH controller. Hence, the biomass of the Control UASB was split over the Test and Control setup to initiate a second start-up (Phase IIIa) during which the organic loading rate and pH was maintained at  $5 \text{ g COD Lr}^{-1} \text{ d}^{-1}$  and  $8$ , respectively. In overlap with Phase IIIa, also the ES of the Test setup was stepwise increased

from 5 to 10 A m<sup>-2</sup> (Phase IIIb) In a final phase (Phase IV), the effect of the ES was investigated under periodically increased nitrogen loading conditions. Therefore, the effect of a working ES of the Test setup was investigated during a period of increased nitrogen loading (Phase IVa), as well as a period where the extra-added nitrogen was again removed from the feed (Phase IVb). Next, this operational procedure was repeated during a period where the ES of the Test setup was switched off (Phase IVc and IVd). Finally, after an adaptation period where the ES was switched on again (Phase IVe), the effect of the ES was investigated during even higher nitrogen loading of up to 2 g N L<sup>-1</sup> extra (Phase IVf and IVg) and where we also allowed the electrochemical cell to control the pH by making advantage of the acidifying anode reaction.

**Table 1** Experimental plan.

Phase	Operation	Period (d)
Ia	Start-up 1	1 – 30
Ib	Gradual increase pH 7 → 8	30 – 70
II	<b>Switch on</b> ES Test setup	70 – 120
IIIa	Start-up 2	130 – 210
IIIb	<b>Switch on</b> ES Test setup	180 – 225
IVa	Add 1 g N L <sup>-1</sup> extra to feed	225 – 238
IVb	Remove extra 1 g N L <sup>-1</sup> from feed	238 – 266
IVc	<b>Switch off</b> ES Test setup + add 1 g N L <sup>-1</sup> extra to feed	266 – 275
IVd	Remove extra 1 g N L <sup>-1</sup> from feed	275 – 287
IVe	<b>Switch on</b> ES Test setup	287 – 303
IVf	Add 1 g N L <sup>-1</sup> extra to feed	303 – 313
IVg	Add 2 g N L <sup>-1</sup> extra to feed + electrochemical acidification (pH 8 → 7)	313 – 340

#### *Sampling and chemical analysis*

Liquid samples were taken 3 times per week of the influent and effluent streams as well as gaseous samples from the headspace. Liquid samples were filtered (0.22 µm) and stored at 4°C for further analysis.

VSS, Kjeldahl nitrogen (Kj-N), ammonium (NH<sub>4</sub><sup>+</sup>), chemical oxygen demand (COD), pH and conductivity were analysed according to standard methods (Greenberg, 1992). Volatile Fatty Acids (VFA) were, after extraction in diethyl ether, analysed with a flame ionization detector (FID) gas chromatograph (GC-2014, Shimadzu). The gas phase composition was analyzed with a Compact GC (Global Analyser Solutions, Breda, The Netherlands), equipped with a Molsieve 5A pre-column and Porabond column (CH<sub>4</sub>, O<sub>2</sub>, H<sub>2</sub> and N<sub>2</sub>) and a Rt-Q-bond pre-column and column (CO<sub>2</sub>, N<sub>2</sub>O and H<sub>2</sub>S). Concentrations of gases were determined by means of a thermal conductivity detector, and were reported at STP (standard temperature and pressure) conditions. Biogas production was measured with a calibrated gas counter.

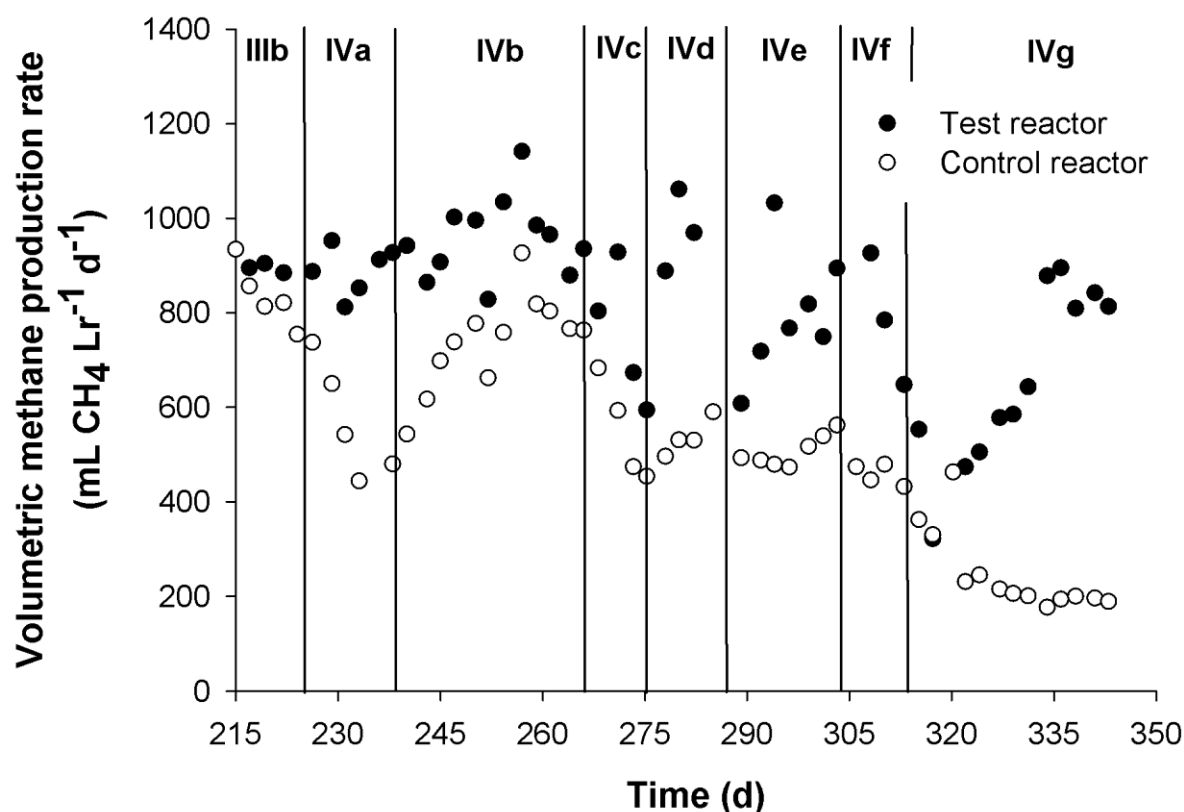
## **Results and Discussion**

After the start-up phase (Phase Ia), the average CH<sub>4</sub> production rate of the Test and Control reactor during Phase Ib was 952±94 and 949±134 mL CH<sub>4</sub> L<sup>-1</sup> d<sup>-1</sup>, respectively. When the ES of the Test setup was switched on at the start of Phase II, an initial decrease in CH<sub>4</sub> production rate of about 20% could be observed. The negative impact on the performance of the microbial community was probably caused by the instantaneous oxygen (7% of the COD

loading rate) and proton production by the anode reaction, in combination with a higher NaOH dosage to counteract acidification. However after 40 days of operation, the Test reactor recovered and reached again the performance of the Control reactor (data not shown).

After the crash of the Test reactor and a second start-up (Phase IIIa and IIIb), both reactors again reached equal performance, with a  $\text{CH}_4$  production rate of  $894 \pm 10$  and  $836 \pm 66$   $\text{mL CH}_4 \text{ L}^{-1} \text{ d}^{-1}$  of the Test and Control reactor, respectively.

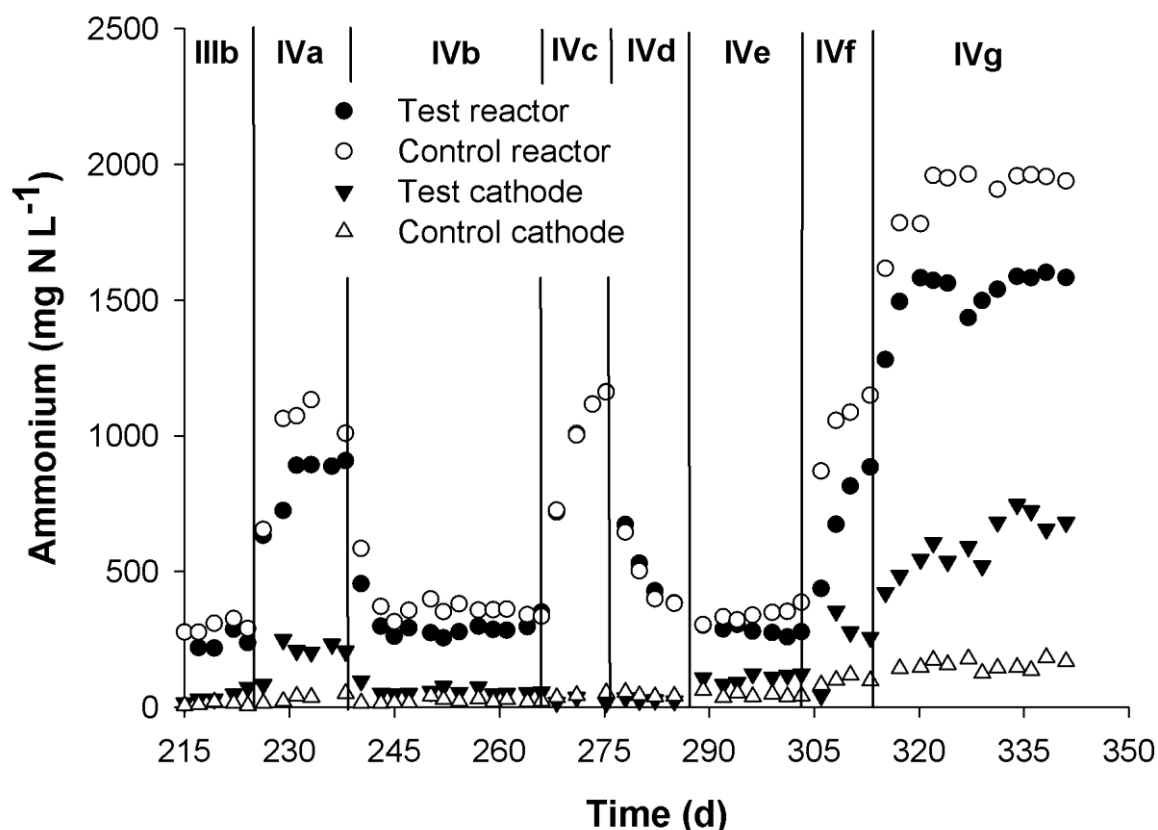
When the nitrogen loading was increased by adding  $1 \text{ g N L}^{-1}$  extra to the feed (Phase IVa), a 43% decrease of the  $\text{CH}_4$  production rate could be observed for the Control reactor, whilst the Test reactor was able to maintain its performance (Fig. 1). Furthermore, the drop in  $\text{CH}_4$  production of the Control reactor coincided with the accumulation of Volatile Fatty Acids (VFA) up to  $2700 \text{ mg COD L}^{-1}$ , whilst no VFA could be detected in the Test reactor (Fig. 3). VFA accumulation is a strong sign of instability, and as described in other studies, this was most probably caused by the high ammonium content (Chen *et al.*, 2008, De Vrieze *et al.*, 2013). By omitting the extra nitrogen from the feed (Phase IVb), the Control reactor was able to recover steadily.



**Figure 1** Volumetric  $\text{CH}_4$  production rate of the Test and Control reactor in function of time. The different phases refer to the experimental plan (Table 1).

Repeating this procedure with a non-working ES of the Test reactor (Phase IVc and IVd) resulted in a decrease in performance of both the Test and Control reactor (Fig. 1). Also this time not only VFA accumulation could be observed in the Control reactor, but also in the Test reactor (Fig. 3). These findings prove that the ES was essential to maintain stability under high nitrogen loading conditions, and can be explained by the fact the  $\text{NH}_4^+$  concentration can be lowered by membrane electrolysis (Fig. 2). Most likely, the corresponding average  $\text{NH}_3$  concentration during Phase IVa in the Test reactor ( $94 \text{ mg N L}^{-1}$ ) did not reach a level that

inhibited the methanogenic community, whereas inhibition might have occurred in the Control reactor were a higher average  $\text{NH}_3$  concentration was present ( $118 \text{ mg N L}^{-1}$ ). Indeed, reported inhibitory  $\text{NH}_3$  concentrations are within a range of 80 to  $150 \text{ mg N L}^{-1}$ , and is dependant on the operational conditions, sludge type and degree of adaptation (Angelidaki and Ahring, 1993). Removal of the extra-added  $\text{NH}_4^+$  from the feed (Phase IVd) caused instantaneous recovery of the Test reactor, whilst the Control reactor seemed to reach an inhibited steady state, which was on average 43% lower in performance compared to the Test reactor.



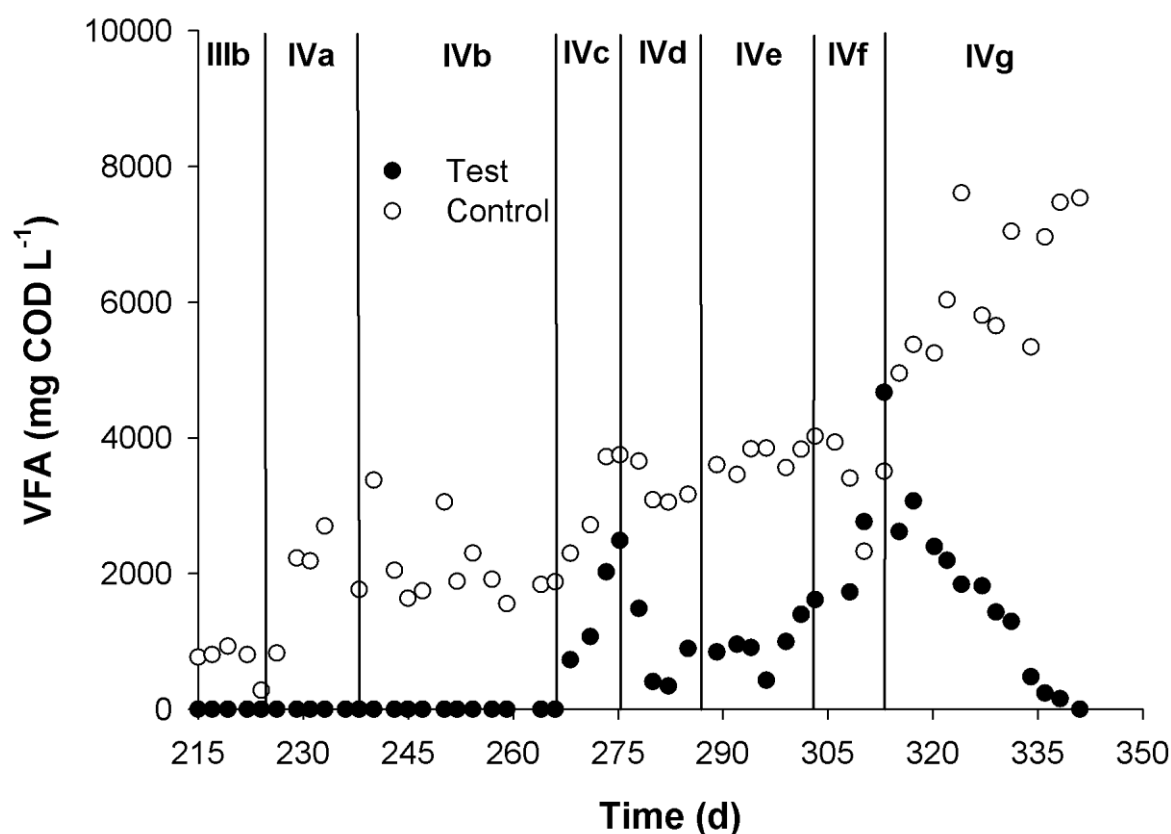
**Figure 2** Ammonium concentration in function of time in the Test and Control reactor (UASB + anode compartment), as well as in the cathode compartments of the Test and Control setup. The different phases refer to the experimental plan (Table 1).

Gradually switching on the ES of the Test reactor from  $5$  to  $10 \text{ A m}^{-2}$  caused again a temporarily negative effect, comparable to Phase II, however this time the recovery took only 16 days (Phase IVe). This shows that gradual increase of the current density is necessary to allow adaptation of the microbial community to the new conditions.

During the final 2 phases (Phase IVf and IVg), the nitrogen loading was again increased by addition of 1 (Phase IVf) and 2 (Phase IVg)  $\text{g N L}^{-1}$  extra to the feed. In contrast to Phase IVa, the  $\text{CH}_4$  production rate of the Test reactor started to decrease dramatically (Fig. 1), and can be explained by the fact that this time also residual VFA was present in the Test reactor (Fig. 3). Further increase of the nitrogen loading ( $2 \text{ g N L}^{-1}$  extra) led to a minimum  $\text{CH}_4$  production rate of  $322 \text{ mL CH}_4 \text{ Lr}^{-1} \text{ d}^{-1}$  at day 317, and was equal to the performance of the Control reactor (Fig. 1). Clearly, the extraction of ammonium by the ES was insufficient to decrease the  $\text{NH}_4^+$  and hence also the  $\text{NH}_3$  concentration below a toxic level (Fig. 2).

Therefore, from day 317 onwards, not only the extraction capacity of the ES was utilised but also the ability to acidify and hence control the pH of the reactor through the use of the

acidifying anode oxidation reaction. Until day 317, the generated protons by the ES were counteracted by NaOH addition in order to operate the Test and Control setup at the same pH. As a result, NaOH addition to the Test reactor was almost double of the Control reactor. This however did not generate a difference in conductivity between both setups, as the extra base addition to the Test reactor was automatically compensated by membrane extraction of the ES. By steadily decreasing the base dosage of the Test reactor up to the level of the Control reactor, the pH of the Test reactor evolved to 7, and as such the acidifying effect of the ES could be investigated. The Test reactor completely recovered up to a  $\text{CH}_4$  production rate of  $856 \pm 38 \text{ mL CH}_4 \text{ L}^{-1} \text{ d}^{-1}$ , whilst the Control reactor remained at a 4.5 times lower production rate of  $192 \pm 10 \text{ mL CH}_4 \text{ L}^{-1} \text{ d}^{-1}$ .

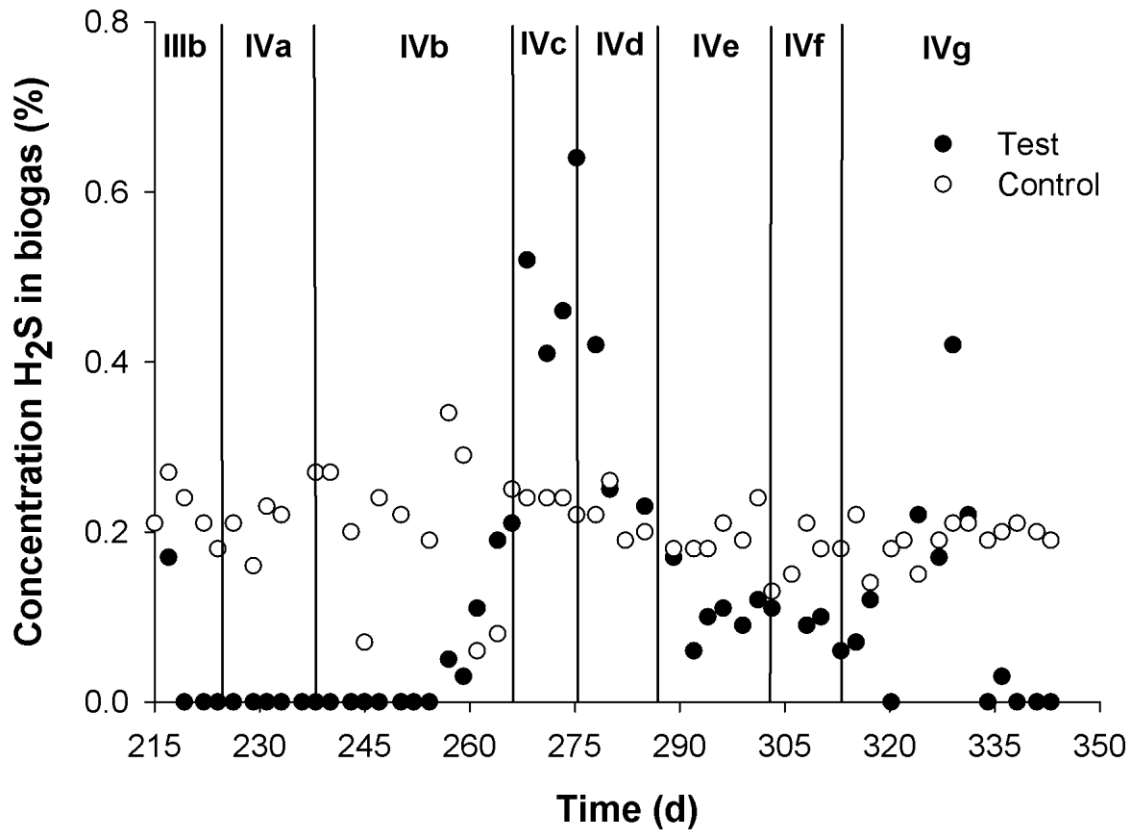


**Figure 3** VFA concentration in the Test and Control reactor in function of time. The different phases refer to the experimental plan (Table 1).

The last phase (Phase IVg) also showed the need for a high ammonium concentration in order to obtain a high extraction efficiency (Fig. 2). In this phase,  $\text{NH}_4^+$  could be extracted at a flux of  $47 \pm 6 \text{ g N m}^{-2} \text{ membrane d}^{-1}$ , resulting in a removal and current efficiency of  $38 \pm 5\%$  and  $28 \pm 2\%$ , respectively. In terms of power input, the nitrogen could be extracted at  $17 \pm 2 \text{ kWh kg}^{-1} \text{ N}$ . The latter is comparable to the results obtained in our previous study where we obtained a power input of  $13 \text{ kWh kg}^{-1} \text{ N}$  at a current density of  $10 \text{ A m}^{-2}$  and  $2 \text{ g N L}^{-1}$  with digestate from a municipal solid waste digester (Desloover *et al.*, 2012).

An interesting side observation during this study was the significantly lower  $\text{H}_2\text{S}$  content in the biogas of the Test reactor when the ES was switched on (Fig. 4). Under these conditions, the  $\text{H}_2\text{S}$  concentration in the biogas of the Test reactor was often below the detection limit (100 ppmv), whilst the  $\text{H}_2\text{S}$  concentration in the Control setup was on average 2000 ppmv. The presence of  $\text{H}_2\text{S}$  constitutes a severe problem to any biogas conversion technology as it

can cause corrosion (Abatzoglou and Boivin, 2009). Hence, electrochemical  $\text{H}_2\text{S}$  removal is a valuable asset next to  $\text{NH}_3$  toxicity control and nutrient recovery.



**Figure 4**  $\text{H}_2\text{S}$  concentration in the biogas of the Test and Control reactor in function of time. The different phases refer to the experimental plan (Table 1).

## Conclusions

From the results obtained in this study we can conclude that:

- An ES is able to control  $\text{NH}_3$  toxicity during anaerobic digestion and hence significantly improve the overall performance and stability through extraction of  $\text{NH}_4^+$  and electrochemical pH control;
- $\text{NH}_4^+$  can be extracted efficiently at reasonable power input in case high  $\text{NH}_4^+$  concentrations in the order of  $\text{g N L}^{-1}$  are present;
- The  $\text{H}_2\text{S}$  emission can be significantly lowered through anodic oxidation of dissolved sulphide species.

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